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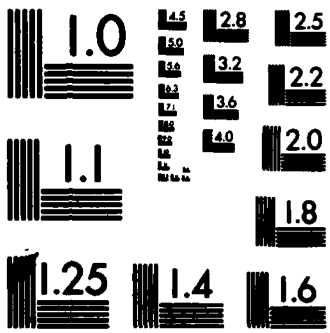

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A single mode cavity microwave sintering apparatus was designed, constructed and utilized to investigate sintering of a number of oxide ceramics. A temperature feedback system was designed and incorporated. Rapid passthrough sintering of β-alumina rods produced high densification rates and fine grain sizes. Mathematical modeling of the loaded cavity was commenced. Through this, it is possible to predict the specimen temperature from non-electrical, dielectric and geometric parameters.

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MICROWAVE SINTERING OF CERAMICS

FINAL REPORT

by

D. Lynn Johnson and M. E. Brodwin
Co-Principal Investigators

FEBRUARY 1984

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CONTENTS

INTRODUCTION

This was an interdisciplinary, initial effort to explore microwave sintering of ceramics. Microwave technology, from the point of view of electrical engineering, was combined with ceramics processing, from the point of view of materials science, to explore this novel processing method. The efforts of the electrical engineering group culminated in a realization of a working microwave system for the simultaneous sintering and in-situ characterization of ceramic rods in the 1000°-2000°C range. Microwave sintering was implemented by a rectangular single mode cavity, and the complete permittivity of rod specimens was deduced by using a variational formulation for its impedance. The system incorporated a feedback control system for maintaining the surface temperature of the rod and a four probe standing wave measuring scheme for dynamic characterization of the specimen.

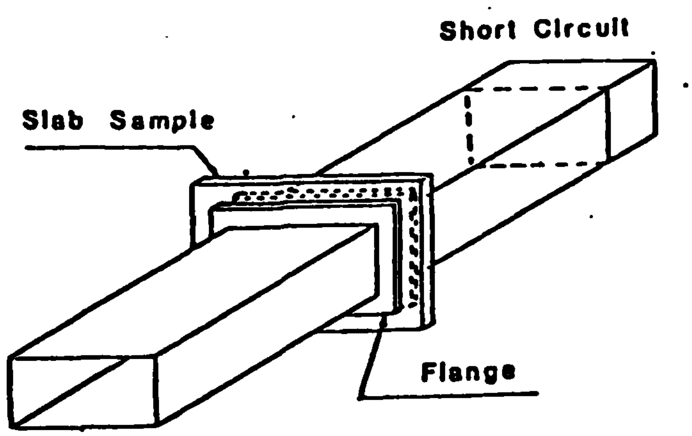
The theory of a rectangular, single mode cavity loaded with a finite rod-shaped specimen was developed, expanding upon the methods of Marcuvitz and Schwinger. The resulting theory is a first step in predicting specimen heating behavior from the electrical and dielectric properties and the characteristics of the applicator.

The cavity applicator was utilized in a study of the sintering of β-alumina and exploratory work in microwave heating of a number of other oxides. Rapid pass-through sintering of β-alumina rods at translation rates through the cavity of 1-4 cm/min produced uniform densification and fine grain size independent of translation rate. Other oxides exhibited behavior ranging from stable heating to extreme runaway conditions and melting.

SYSTEMS DESIGN

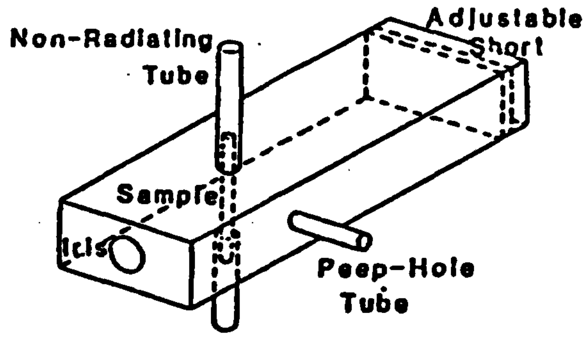
It was decided at the outset to investigate single mode applicators rather than the multimode oven-type cavities, since the latter are susceptible of temperature instabilities, energy density inhomogeneities, and in general, are more difficult to control and describe quantitatively. Moreover they are amenable only to batch processing, and it was desired to investigate rapid pass-through sintering.

The applicators were fashioned from a section of rectangular waveguide. The simplest of these is the slab applicator shown below, which consists of a thin slab of material inserted transverse to the waveguide, with the waveguide terminated by a moveable short circuit. The energy flows from the left, and the amount of energy absorbed by the slab is controlled by the position of the short circuit. An essential feature of this applicator is the non-contacting adjustable short circuit which was designed and constructed. A 90° bend in the waveguide leading to the applicator incorporated a viewing port for observing the slab specimen or measuring its temperature with an optical pyrometer.



Slab applicator

A more complicated applicator in which rod and tube-shaped specimens can be heated is shown below. This is similar to a single mode applicator discussed by Berteaud and Badot[1]. The energy is coupled into the applicator through an iris, and the adjustable short is used to tune it. Non-radiating tubes were soldered to all penetrations of the waveguide in order to prevent microwave leakage. The specimens were fed through tubes in the broad walls while the specimen was observed and temperature was measured through tubes in the narrow walls. The specimens were rotated and translated through the applicator at controlled velocities.



Rod and tube applicator

Initially, we fabricated a set of iris plates consisting of thin sheets of brass in which various sizes of holes had been cut. It was found that various materials required different iris diameters for optimum heating and, in fact, as heating and sintering took place the optimum iris size would change. It was a slow process to change irises to find the optimum size, and it was impossible to change the iris during sintering. Therefore, we designed and constructed a simple adjustable aperture which consisted of sliding brass sheets normal to the waveguide. Unfortunately, extensive arcing occurred between the sheets and the waveguide. To circumvent the arcing problem an E-plane T-coupler was designed and tested, initially at X-band, taking advantage of existing diagnostic equipment at this frequency. Subsequently, a T-coupler was constructed and utilized for part of the studies. However, the power transmission was not satisfactory, and it was abandoned.

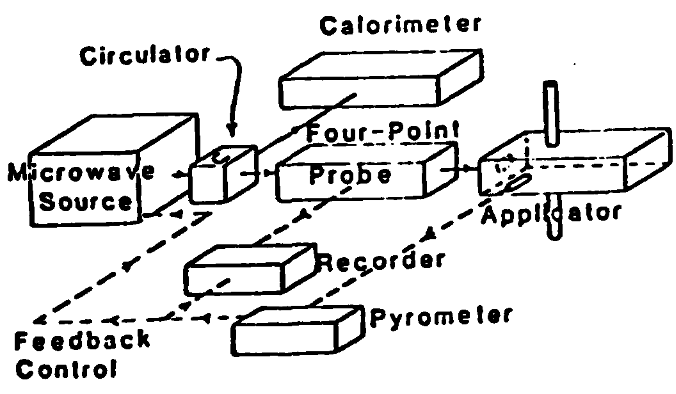
A new adjustable aperture, incorporating chokes, was designed, constructed, and put into operation successfully. No arcing was observed even at full power (850 W). It has greatly enhanced the ease of operation of the system and has, moreover, made it possible to quickly adjust to a wide range of material properties.

A temperature control system was designed, constructed, and placed in operation. The output of an optical pyrometer system was input to a control circuit we designed and built which controlled the output power of the microwave source to maintain the surface temperature of the sample at a preset value.

To fully understand and develop theories for the heating of a sample, it is necessary to monitor the reflections from the applicator. The usual technique is to place a fine wire into the waveguide ahead of the applicator through a slot cut in the center of the upper broad wall. The standing wave in front of the iris is detected by sliding this probe along the main axis of the waveguide. Although this is satisfactory for stable operating conditions, it is completely inadequate for sintering studies in which the temperature and the properties of the specimen are changing rapidly, at least initially. To sense these almost instantaneous changes, it was necessary to develop a new apparatus. Four stationary probes were inserted into the waveguide at appropriate positions so that their output completely determined the standing wave pattern. A circuit was designed, constructed and installed which transforms the output of these probes into the real and imaginary parts of the reflection coefficient, and these are plotted on an x-y plotter (a Smith plot results as the short circuit is translated). By the use of this instrumentation, we are able to completely determine the reflection properties of the applicator and sample under any conditions, and to use these results in conjunction with the theories being developed to understand the properties and evolution of properties of the samples during sintering. With the four-point probe, the adjustable iris, and the adjustable short circuit, it is possible, in just a few minutes, to optimize the coupling and the tuning of the applicator to any material of interest.

A circulator was built into our system to enhance stability and also to protect the magnetron in the source. Reflected energy from the applicator system is directed by means of the circulator to a calorimeter where it is absorbed. The calorimeter was used to measure the reflected power as an independent check of the four-point probe system.

A block diagram of the system is illustrated below. This complete system is a very powerful tool for studying microwave heating and sintering for a wide variety of materials under a wide variety of conditions.



Microwave sintering system

Our original plans included automating the coupling and tuning of the applicator. Some initial progress has been made. A servo mechanism for controlling the position of the adjustable short-circuit was designed, and an X-band model was constructed and tested. Initially, a signal from a single probe was used, but it became apparent that this was inadequate. The output of the four probe system, constructed later, on the other hand, would be suitable for this mechanism. Future plans included interfacing a microcomputer to this system to facilitate automatic tuning and coupling of the cavity through this servo drive mechanism.

SINTERING OF CERAMICS

Preliminary attempts were made at sintering a variety of ceramic materials with a wide spectrum of results ranging from non-heating to nearly instantaneous shattering due to thermal shock.

The slab applicator was employed to investigate the heating and sintering of Alcoa β-alumina sheets. The specimens were in the range of 0.5-2.0 mm thick, and were prepared by tape casting. The results on transient heating response of the slabs suggested that internal temperatures were higher than the surface temperature. Steady state experiments indicated that thinner slabs achieved lower steady state temperatures at the same generator output power. This is a consequence of a smaller generated heat due to the smaller volume of thinner slabs. Deduced values of σ and ε_r of the β-alumina agreed in the order of magnitude and temperature dependence with published results.[2] However, the temperature of the slab was not uniform across its face, but was higher near the center. This is not a surprising result since the energy density in the waveguide is greatest at the center.

A systematic investigation of the sintering of Alcoa β-alumina in the rod applicator was conducted. Rods approximately 5 mm in diameter were isostatically pressed and presintered at 600°C to burn out the binder. Reference marks were inscribed along the length of the rods so that axial and radial shrinkage could be measured. These rods were passed through the applicator, while being rotated, at speeds of 1-4 cm/min. The effective height of the applicator was reduced to 2.5 cm by the insertion of brass tubes through the specimen insertion non-radiating tubes. Thus, the microwave radiation was incident upon the specimens over a distance of 2.5 cm. The maximum surface temperature of the specimen occurred at the point where the specimen exited this region. All of the runs were made with a 66 mm square coupling aperture, 835 W of microwave power input to the applicator, and air atmosphere. The short circuit was adjusted for minimum reflection.

The maximum surface temperature of the specimens was approximately 1500°C and was more or less independent of the rate of translation of the specimens. Thus the overall heating rate of the specimens at 4 cm/min translation rate was approximately 40°C/s, although the maximum heating rate was considerably in excess of this since the temperature profile was not linear. Stable operation could not be maintained at speeds greater than 4 cm/min as the hot zone was pushed out of the radiation field.

The average linear shrinkage of the specimens was approximately 9%, independent of the translation rate. The final density was approximately 92% of theoretical, and the final grain size was about 4 μm, both independent of translation rate. The relatively low density is undoubtedly a function of the nature of the starting powder. Nevertheless, it is interesting to note that although the densification rate increased remarkably as the speed increased, the final density remained constant.

Microwave sintering of $BaTiO_3$, TiO_2, ZrO_2, ZnO, and NiO was surveyed. Significant difficulty was encountered in controlling the heating of $BaTiO_3$. With the appropriate aperture in place, the heating was almost instantaneous with the result that the rod specimen was fractured somewhat violently. This perhaps represents the extreme of runaway phenomena that can occur with microwave heating. It occurs when the absorbed microwave power causes additional absorption through the temperature rise. With power absorbed throughout the rod but dissipated only from the surface, the center of the specimen can become heated very rapidly under some circumstances.

The sintering of ZrO_2 is a less extreme example. In this case the material could be heated readily to the melting point in the interior of the rod, but at a more controlled rate and without rupture of the rod. However, it was felt that this was not a fruitful material for our preliminary investigations because of its tendency to melt.

In the first attempts to sinter TiO_2, a runaway phenomenon was observed, including specimen melting. However, rod specimens could be successfully heated by slowly increasing the microwave power. Upon gradual application of power a point was reached at which the center of the rod suspended in the applicator became heated to incandescence. An unexpected transient heating phenomenon was then observed. The heated zone began to spread and then the central region of the rod began to cool down, resulting in two separated hot zones. These hot zones propagated out of the applicator and then cooled. As additional power was added, this phenomenon was repeated several times. There are apparently transient changes occurring in the material during heating that alter its ability to absorb microwave energy.

Zinc oxide not only absorbs microwave energy very strongly, but propagates it, as well, probably because of its electrical conductivity. Rods of length greater than the cavity height were heated along their entire length, which implies that the energy was transmitted along the rod lengths.

We have discovered that optimum heating of zinc oxide depends upon the extent of densification. The maximum percent of absorbed power for isostatically pressed and presintered (600°C) ZnO rods occurred with the short circuit located 0.7 λ from the sample, where λ is the wavelength of the microwave radiation in the waveguide. As a sample became hot, and sintering proceeded, it was necessary to move the short circuit continuously to just over 0.9 λ in the fully sintered condition to effect maximum power absorption.

A significant difference in the heating of two ceramics has been discovered. The maximum absorbed power for sintered zinc oxide occurred at a short circuit position of just over 0.9 λ from the specimen, as noted above, while it was at 0.83 λ for β-alumina. This means that the maximum heating of zinc oxide occurred near the maximum in the magnetic component of the field, while β-alumina was heated optimally with a larger electrical field intensity component. Control of the position of the electrical and magnetic field components with respect to the specimen is easily effected by changing the position of the short circuit. This result represents one of the advantages of heating at microwave frequencies as compared to dielectric and induction heating frequencies.

Initial attempts were made to sinter NiO using reagent grade powder. This was not a very sinterable powder. The maximum temperature achievable with a fixed iris was in the range of 1100°C. At this point the adjustable coupling iris was installed. With the aperture fully open the applicator was over-coupled. By adjusting the iris opening, the critical coupling condition could be easily attained. As the coupling became adjusted properly the sample became incandescent, resulting in a change in properties and an under-coupled condition. Continued adjusting of the coupling aperture brought the cavity again to critical coupling, which permitted heating the sample to very high temperatures. The significant utility of the present system was readily demonstrated by this exercise. To review, the four point probe sensed the standing wave ratio, indicating the reflection coefficient from the applicator. The adjustable iris permitted the coupling to be optimized and the adjustable short made it possible to tune the cavity. By these two adjustments, the heating of the specimen could be optimized. By this means, the specimen temperature could be maximized, relfected energy minimized, and the efficiency of coupling of the microwave energy with the specimen was optimized.

Since reagent grade NiO was not very sinterable, a more sinterable powder was prepared by calcining $NiCO_3$ at a variety of temperatures. It was possible to obtain NiO at calcining temperatures of 300°C and higher, but the low temperature calcined materials fractured upon application of microwave energy. After experimenting, it was ascertained that a 700°C calcine provided a sinterable material which could be heated successfully and reproducibly to the sintering temperature.

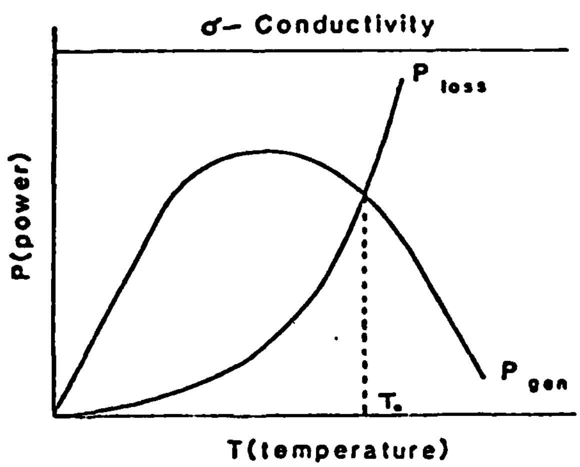
THEORY

There are three goals to the theoretical understanding of microwave applicators. The most immediate one is to develop a theory for the temperature of a sample as a function of frequency and all known material and geometry parameters. The second goal is to devise an analysis for the temperature distribution as a function of time at every point within the sample during heating or during translation of the sample with a steady temperature profile within the applicator. The final goal is to derive relationships which enable one to utilize the apparatus for in-situ characterization of the sample, that is, utilizing the observed reflection information to obtain the conductivity and permittivity of the sample.

The first goal has been approached by assuming that the conductivity of the sample is such that all power absorbed in the applicator is dissipated as heat in the sample. Once the power absorbed by the sample is known, then by means of the heat equations one can determine the temperature. One finds the stable operating temperature by equating the heat loss to the absorbed power. The theoretical absorbed power can be determined by calculating the reflection coefficient, ρ, of the applicator, and using the following equation:

$$P_{abs} = P_a \ (1 - |\rho|^2)$$

here P_a is the available power from the microwave source. For materials whose conductivity increases with temperature, the power absorbed in the specimen and power loss curves are shown qualitatively below. Stable operation



Power absorbed and lost

would obtain if the power loss and power absorbed curves cross in the downward-branch of the latter, as shown in this figure. The temperature of the specimen would be unstable if the power loss curve crossed the power absorbed curve on the upward branch of this curve. The center of the sample is hotter than the surface, and if the center absorbs more power than the surface because of its higher temperature, a thermal runaway will occur.

These ideas were incorporated into a model of the thin slab applicator such as that described above.

If the temperature dependence of the conductivity and permittivity are known, then the reflection coefficient can be calculated for each value of temperature and, therefore, the power absorbed curve versus temperature can be determined. By using published values of the conductivity and permittivity of β-alumina, we obtained reasonable agreement with the observed stable temperature.

The calculations are significantly more complicated in the case of the rod applicator. The electromagnetic description of the short circuit and the iris is straightforward, but that of the rod is much more complex. The reflecting properties of a small rod with a uniform conductivity and permittivity were developed by Schwinger, and then elaborated by Marcuvitz.[3] The reflection coefficient can be found using the Marcuvitz calculations. It was realized that a more accurate model was needed to remove the limitations on rod diameter and occurrence of rod resonance associated with the Marcuvitz model. An improved model, using the same Schwinger variational formulation that Marcuvitz used, was therefore derived and implemented in the analysis of the experimental data, and the characterization of the rod samples of β-alumina ZnO and NiO. In addition, an equivalent, exciting wave approach for calculating the total electric field intensity inside the rod was formulated and used. The detailed analysis of the experimental results on optimum heating conditions, temperature profile control, transient heating characteristics, and the experimental determination of the variation of complex permittivity of β-alumina, ZnO and NiO with temperature are presented in the Ph.D. dissertation of J. C. Araneta. In addition, a theoretical analysis of thermal stability and stable temperature is also presented there.[3]

The third goal is to be able to characterize the material at the same time that it is being sintered. Our analysis shows that if the reflection coefficient and the surface temperature are measured during the sintering process, the use of the first term of the Schwinger-Marcuvitz theory would enable us to determine an equivalent, uniform conductivity and permittivity. To be able to determine non-uniform characteristics requires a further expansion of the theory to include additional higher order terms. These aspects of the theory are under investigation. We have at the present time established the relationship between reflection coefficient and conductivity, and are extending the theory to develop more accurate accurate relationships for non-uniform parameters.

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